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Journées Équations aux dérivées partielles (1989), p. 1-10

http://www.numdam.org/item?id=JEDP_1989____A10_0

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Asymptotic Behavior of the Ground State of Large Atoms

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June 12, 1989

Abstract

We review some results on the behavior of the ground state energy and the ground state density for large atoms as the nuclear charge Z increases to infinity. Here the atom is described by various models, namely the Thomas-Fermi, the Thomas-Fermi-Weizsäcker, the Fermi-Hellmann, the Hellmann-Weizsäcker model, and the Schrödinger equation.

1 Introduction

The following results for large atoms, i.e., for large nuclear charge Z and large electron number N keeping the ratio $Z/N = \alpha$ fixed, shall be presented:

- Asymptotic behavior of the ground state energy,
- Bounds on the excess charge,
- Asymptotic behavior of the ground state density.

The results will be presented in the context of the following models ordered roughly according to increasing complexity:

1. The Thomas-Fermi model (Thomas [20], Fermi [7, 6]):

$$\mathcal{E}_{TF}(\rho) = \int \frac{3}{5} \left(\frac{6\pi^2}{q} \right)^{2/3} \rho(r)^{5/3} - \frac{Z}{|r|} \rho(r) + \frac{1}{2} (\rho * \frac{1}{|\cdot|})(r) \rho(r) d^3r \quad (1)$$

$$\rho \geq 0, \quad \int \rho \leq N, \quad (2)$$

q being the number of spin states of one electron, i.e., $q=2$.

2. The Thomas-Fermi-Weizsäcker model (von Weizsäcker [21]):

$$\mathcal{E}_{TFW}(\rho) = \int (\nabla \sqrt{\rho(r)})^2 + \mathcal{E}_{TF}(\rho) \quad (3)$$

with the conditions (2).

3. The Fermi-Hellmann model (Fermi [7], Hellmann [8]):

$$\begin{aligned} \mathcal{E}_H(\underline{\rho}) = & \sum_{l=0}^{\infty} \int_0^{\infty} \frac{3}{5} \left(\frac{\pi}{2(q + \frac{1}{2})} \right)^2 \rho_l(r)^3 + \left(\frac{(l + \frac{1}{2})^2}{r^2} - \frac{Z}{r} \right) \rho_l(r) dr \\ & + \frac{1}{2} \sum_{l,l'=0}^{\infty} \int_0^{\infty} \int_0^{\infty} \frac{\rho_l(r)\rho_{l'}(r')}{\max\{r, r'\}} dr dr', \end{aligned} \quad (4)$$

$$\rho_l \geq 0, \quad \sum_{l=0}^{\infty} \int_0^{\infty} \rho_l(r) dr \leq N. \quad (5)$$

4. The Hellmann-Weizsäcker model (Hellmann [8])

$$\mathcal{E}_{HW}(\underline{\rho}) = \sum_{l=0}^{\infty} \int_0^{\infty} \sqrt{\rho_l} r^2 - \frac{1}{4r^2} \rho_l dr + \mathcal{E}_H(\underline{\rho}) \quad (6)$$

with condition (5).

5. The Schrödinger model

$$E_Q(Z, N) = \inf\{(\psi, H\psi) | \psi \in Q(H), \|\psi\| = 1\} \quad (7)$$

where

$$H = \sum_{i=1}^N \left(-\Delta_i - \frac{Z}{|\mathbf{r}_i|} \right) + \sum_{\substack{i,j=1 \\ i < j}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (8)$$

as self-adjoint realization on $\bigwedge_{i=1}^N (L^2(\mathbb{R}^3) \otimes \mathbb{C}^q)$.

We remark that basic properties of the first four models – such as existence of minimizers in suitable functions spaces – are well known (Lieb [12] and Siedentop and Weikard [15]). – We shall mention some more results for the models 1, 2, 4, and 5 but shall concentrate mainly on the Fermi-Hellmann equations.

2 Asymptotic Behavior of the Ground State Energy

Denote the infima of the functionals by roman E – the functionals are denoted by caligraphic \mathcal{E} . With this notation we can formulate the following results:

1.

$$E_{TF}(Z, N) = E_{TF}(1, \alpha)Z^{7/3} \quad (9)$$

where $\alpha = Z/N$. This is immediate by scaling, i.e., choosing $\rho(r) = Z^2 \rho_1(Z^{1/3}r)$ in (1) (Fermi [6]). In particular, the Thomas-Fermi energy behaves exactly proportional to $Z^{7/3}$, if α is fixed.

2.

$$E_{TFW}(Z, N) = E_{TF}(Z, N) + DZ^2 + o(Z^2) \quad (10)$$

for fixed α where $D = \frac{q}{3\pi^2} I_1$ and $I_1 = \int (\nabla\psi)^2 \approx 8.583897$, ψ being the positive solution of

$$\left(-\Delta + \left(\frac{6\pi^2}{q} \right)^{2/3} |\psi|^{4/3} - Z|\cdot|^{-1} \right) \psi = 0 \quad (11)$$

(Lieb [12]).

3.

$$E_H(Z, Z) = E_{TF}(Z, Z) + O(Z^{5/3}) \quad (12)$$

(Siedentop and Weikard [17], Weikard [22]).

We indicate the proof of (12). To this end we observe some facts for the Fermi-Hellmann model: The minimizer of \mathcal{E}_H fulfills the Euler-Lagrange equation

$$\rho_l(r) = \frac{2q(l + \frac{1}{2})}{\pi} \left[\varphi(r) - \frac{(l + \frac{1}{2})^2}{r^2} \right]_+^{1/2} \quad l = 0, 1, 2, \dots \quad (13)$$

$$\varphi(r) = \frac{Z}{r} - \sum_{l=0}^{\infty} \int_0^{\infty} \frac{\rho_l(r')}{\max\{r, r'\}} dr'. \quad (14)$$

Moreover by Legendre transform the dual variational principle of the Hellmann principle is

$$\mathcal{F}_{Z, \mu}^H(\psi) = -\frac{1}{2} \int_0^{\infty} (r\psi)^2 dr - \frac{2}{3} \sum_{l=0}^{\infty} \frac{2q(l + \frac{1}{2})}{\pi} \int_0^{\infty} \left[\psi(r) - \frac{(l + \frac{1}{2})^2}{r^2} + \mu \right]_+^{3/2} dr \quad (15)$$

with $(r\psi)' \in L^2(\mathbb{R}^+)$, $r\psi(r) \rightarrow Z$ for $Z \rightarrow 0$, and $\psi(r) = O(1/r)$ as $r \rightarrow \infty$. For the supremum $F_H(Z, \mu)$ of this functional we have

$$F_H(Z, \mu) + \mu N = E_H(Z, N); \quad (16)$$

$$N = \sum_{l=0}^{\infty} \frac{q2(l + \frac{1}{2})}{\pi} \int_0^{\infty} \left[\psi_{max}(r) - \frac{(l + \frac{1}{2})^2}{r^2} + \mu \right]_+^{1/2} dr,$$

where ψ_{max} is the maximizer of (15).

For the proof of (12) one chooses

$$\psi(r) = \varphi_{TF}(r) = \frac{Z}{r} - \int_0^\infty \frac{\rho_{TF}(r')}{|r-r'|} d^3r' \quad (17)$$

for the lower bound, where ρ_{TF} is the minimizer of \mathcal{E}_{TF} , in the lower bound and ρ_l as in (13) substituting φ , however, by φ_{TF} . The result follows then from the fact that the minimizer of \mathcal{E}_H has always particle number $\int_0^\infty \sum_{l=0}^\infty \rho_l(r) dr$ smaller than Z (see Section 3), i.e., we use allowed trial functions, and the explicit summation over the angular momenta l . This may be done by Poisson summation or more directly by using a convexity argument (see equation (39) for a similar result).

4.

$$E_{HW}(Z, Z) = E_{TF}(Z, Z) + O(Z^2) \quad (18)$$

(Siedentop and Weikard [18, 17, 16]).

5.

$$E_Q(Z, N) = E_{TF}(Z, N) + \frac{q}{8} Z^2 + O(Z^{47/24}) \quad (19)$$

where $Z/N = \alpha$ is fixed.

This has been conjectured by Scott [14]. The first term was established by Lieb and Simon [13]. The proof of (19) has been given by Siedentop and Weikard [17, 16] (see also Hughes [9] for the lower bound) for the neutral case and has been extended to general α by Bach [1].

We wish to outline the proof for $Z = N$. A lower bound may be obtained by an estimate on the indirect part of the Coulomb energy (Lieb [11]). It turns out that

$$E_Q(Z, Z) \geq Z^{4/3} \inf \sigma \left(\sum_{i=1}^N h_{TF,i} \right) - \frac{1}{2} \int \rho_{TF} * |\cdot|^{-1}(r) \rho_{TF}(r) d^3r + O(Z^{5/3}) \quad (20)$$

$$h_{TF,i} = \underbrace{1 \otimes \dots \otimes 1}_{i-1 \text{ factors}} \otimes h_{TF} \otimes \underbrace{1 \otimes \dots \otimes 1}_{N-i \text{ factors}}$$

$$h_{TF} = -Z^{-2/3} \Delta + \varphi_{TF,1} \quad (21)$$

where $\varphi_{TF,1}$ is the Thomas-Fermi potential (17), however for $Z = 1$. Thus the first summand on the right hand side of (20) may be estimated from below by $Z^{4/3}$ times the sum of all negative eigenvalues of h_{TF} . We observe that (21) can be broken up into a set of uncoupled ordinary differential equations (decompositon into angular momentum channels). A carefull WKB analysis for high angular momenta and summing up the “bare” Coulomb eigenvalues for low angular momenta yields the answer up to errors of order $Z^{17/9} \log Z$.

The upper bound may be obtained by choosing an appropriate “trial” operator d_1

$$0 \leq d_1 \leq 1, \quad d_1 \in \mathcal{I}_1(L^2(\mathbb{R}^3) \otimes \mathbb{C}^q), \quad \text{tr } d_1 \leq N, \quad (22)$$

a so called one-particle density matrix in the inequality

$$E_Q(Z, N) \leq \text{tr} [(-\Delta - Z/|\cdot| + \frac{1}{2}V)d_1] \quad (23)$$

where $V = \rho * |\cdot|^{-1}$, ρ being the density of d_1 , i.e., formally $\rho(r) = \sum_{\sigma=1}^q d_1(r, \sigma, r, \sigma)$. After some intermediate steps one obtains

$$E_Q(Z, Z) \leq \mathcal{E}_H(\underline{\rho}) + \frac{q}{8}Z^2 + O(Z^{47/24}). \quad (24)$$

Equation (12) completes the proof.

3 Bounds on the Excess Charge

Let E denote any of the above energies

$$N_c = \inf\{N | E(Z, N) = E(Z, N + k) \text{ for all } k \in \mathbb{N}\} \quad (25)$$

The maximal excess charge is then $Q_c = N_c - Z$. It may be easily shown that Q_c is nonnegative in all of the above models. In the following we wish to discuss some upper bounds on Q_c .

- The Thomas-Fermi and Fermi-Hellmann model:

$$Q_c^{TF} = Q_c^H = 0$$

(Lieb and Simon [13], Siedentop and Weikard [15]). Here we indicate the proof of this result for the Fermi-Hellmann case. Let ρ_1, ρ_2, \dots be the absolute minimizer of the Fermi-Hellmann functional. Assume $N_c \leq Z$. Then

$$\begin{aligned} Z &> N_c = \int_0^\infty \sum_{l=0}^\infty \rho_l dr = \sum_{l=0}^\infty \frac{q2(l+1/2)}{\pi} \int_0^\infty \left[\varphi(r) - \frac{(l+1/2)^2}{r^2} \right]_+^{1/2} dr \\ &\geq \frac{q}{\pi} \int_0^\infty \left[\frac{Z - N_c}{r} - \frac{1}{4r^2} \right]_+^{1/2} dr = \infty \end{aligned} \quad (26)$$

which is a contradiction. On the other hand assume $N_c > Z$. Then there is an R such that $\varphi(r) < 0$ for $r > R$. Then $(r\varphi)'' = 0$ in this region, i.e., $\varphi(r) = a + \frac{b}{r}$. Since $\varphi(\infty) = 0$ the constant a is zero and b negative. Because of the continuity of φ , $\varphi(r) < 0$ on \mathbb{R}^+ which cannot hold. The Thomas-Fermi case can be treated analogously.

- For the Thomas-Fermi-Weizsäcker model one has

$$Q_c^{TFW} \leq 178.03 \frac{q}{6\pi^2} \quad (27)$$

(Benguria and Lieb [3], Solovej [19]) This bound is obtained by an universal (Z independent) bound on the potential and a bound on the density in terms of the potential.

- In the quantum mechanical case the following bounds are known

$$Q_c^q \leq Z \quad (28)$$

(Lieb [10]) and

$$Q_c^q = O(Z^{47/56}) \quad (29)$$

(Fefferman and Seco [5, 4]). The proof of (29) uses (19) together with the fact that the nucleus is screened out already at small distances.

4 Asymptotic Behavior of the Ground State Density

Let $d = \frac{18\pi}{q}$. Then:

- Thomas-Fermi model:

$$\varphi_{TF}^Z(r) \leq \min\left\{\frac{d^2}{r^4}, \frac{Z}{r}\right\} \quad (30)$$

for $Z, r > 0$, where φ_{TF}^Z is the Thomas-Fermi potential for charge Z . Moreover, φ_{TF}^Z is monotone in Z and the limiting function is

$$\varphi_{TF}^\infty(r) = \frac{d^2}{r^4} \quad (31)$$

This follows immediatly from comparison arguments.

- Thomas-Fermi-Weizsäcker model:

In this subsection we use units such that the constant in front of the $\rho^{5/3}$ term in (3) is $3/5$.

$$\varphi_{TFW}^Z(r) \leq \chi(\alpha)r^{-4} + \frac{\pi^2}{\alpha^2}r^{-2} \quad (32)$$

where χ is given as

$$\chi(\alpha) = \begin{cases} 9\pi^{-2} + c\alpha^{\tau-4} & 0 \leq \alpha \leq \alpha_0 \\ 25\pi^{-25}(1-\alpha)^{-4} & \alpha_0 < \alpha < 1 \end{cases}$$

and (C, α_0) is chosen such that χ is $C^1([0, 1])$ and $\tau = \frac{1}{2} + \frac{\sqrt{73}}{2}$. (Benguria and Lieb [3], Solovej [19])

$$\varphi_{TFW}^Z(r) \rightarrow \varphi_{TFW}^\infty(r) \quad (33)$$

and

$$\varphi_{TFW}^\infty(r) = 9\pi^{-2}r^{-4} - \frac{27}{4}r^{-2} - \frac{25}{64}\pi^2 - \frac{37}{768}\pi^4r^2 + O(r^{-\frac{1}{2} + \frac{\sqrt{73}}{2}}). \quad (34)$$

Solovej obtains also the corresponding limit for the density.

- Fermi-Hellmann model:

The following results are from Bach and Siedentop [2].

$$\varphi_H^Z(r) \leq \min \left\{ \frac{Z}{r}, \left(\frac{d}{r^2} + \frac{1}{2r} \right)^2 \right\} \quad (35)$$

There exists some R such that for $r \geq R$ we have

$$\varphi_H^Z(r) \geq \frac{1}{4r^2}. \quad (36)$$

$\varphi_H^Z(r)$ is monotone increasing in Z

$$\varphi_H^\infty(r) = \frac{d^2}{r^4} + O(r^{-5/2}) \quad \text{at } 0, \quad (37)$$

and

$$\varphi_H^\infty(r) = \frac{1}{4r^2} + o(r^{-2}) \quad \text{at } \infty. \quad (38)$$

The first inequality in (35) is immediate by writing φ_H^Z in terms of ρ_l . To prove the second inequality we use the following lemma

$$-\frac{1}{3} \left(\eta - \frac{1}{4} \right)_+^{3/2} \leq \sum_{l=0}^{\infty} \eta \left(l + \frac{1}{2} \right) \left[1 - \left(\eta \left(l + \frac{1}{2} \right) \right)^2 \right]_+^{1/2} \eta - \frac{1}{3} \leq \frac{5}{4} \eta^{3/2} \quad (39)$$

The proof of (39) uses convexity of $x(1-x)_+^{1/2}$ for $0 \leq x \leq 1$ and a careful estimate of the error term arising at 0 and 1. (39) yields the following differential inequality for the solution φ of (5)

$$\begin{aligned} & -\frac{1}{r}(r\varphi)'' + \frac{2q}{3\pi}\varphi^{3/2} - \frac{1}{3}r^{-1/2}\varphi^{3/4} \left(1 - \frac{r\varphi^{1/2}}{4} \right)_+ \\ & \leq -\frac{1}{r}(r\varphi)'' + \sum_{l=0}^{\infty} \frac{q(2l+1)}{\pi r^2} \left(\varphi(r) - \frac{(l+\frac{1}{2})^2}{r^2} \right)_+^{1/2} \\ & \leq -\frac{1}{r}(r\varphi)'' + \frac{2q}{3\pi}\varphi^{3/2} + \frac{5}{4}r^{-1/2}\varphi^{3/4} \end{aligned} \quad (40)$$

This allows the second function of the right hand side of (35) as comparison function, which proves (35).

The monotonicity of φ_Z in Z is immediate by comparison. The convergence of φ_Z to φ_∞ follows also immediatly.

To obtain (37) we use the comparison function

$$\frac{1}{dr} + \frac{2d^{1/2}}{r^{5/2}} + \frac{d^2}{r^4} \quad (41)$$

with $c = \left[\frac{27}{38} + \left(\left(\frac{27}{38} \right)^2 - \frac{2}{9} \right)^{1/2} \right]$ for the bound from above and

$$\varphi_{TF}(r) - \frac{5}{4} r^{-5/2} \left(d + \frac{r}{2} \right)^{1/2} \quad (42)$$

as the comparison function from below. By the limiting function for the Thomas-Fermi model (31) the equation (37) follows. Equation (38) follows from (35) and the following observations. Suppose there was a radius R such that $\sum_{i=0}^{\infty} \rho_i(r) = 0$ for r bigger than R . Denote by R the minimum over all such R . Since

$$\varphi(r) = \frac{Z}{r} - \int_0^\infty \frac{\sum_{i=0}^{\infty} \rho_i(r')}{\max\{r, r'\}} dr' \quad (43)$$

$\varphi(R) = 0$. Because of the continuity of φ we can choose a δ such that for all x with $|x - R| < \delta$, $|\varphi(x)| < 1/8R^2$ holds. Thus ρ_0, ρ_1, \dots is zero also to the left of R , which is a contradiction. Thus there exists a sequence r_n such that $r_n \rightarrow \infty$ and $\varphi(r_n) \geq 1/4r_n^2$. Now use a comparison between r_n and r_{n+1} with comparison function $1/4r^2$ to obtain the result.

- The Schrödinger equation

Let ρ_Q be the ground state density, i.e.,

$$\rho_Q^Z(r) = N \int dr_1^3 \dots dr_N^3 \sum_{\sigma_1, \dots, \sigma_N=1}^q |\psi_Z(r, \sigma_1, r_2, \sigma_2, \dots, r_N, \sigma_N)|^2 \quad (44)$$

where ψ_Z is the ground state of (8). Let ρ_{TF} be the Thomas-Fermi density for charge 1, Ω a measurable set in \mathbb{R}^3 . Then

$$\int_{\Omega} Z^{-2} \rho_Q^Z(Z^{-1/3}r) d^3r \rightarrow \int_{\Omega} \rho_{TF}(r) d^3r \quad (45)$$

holds (Lieb and Simon [13]).

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